Solar STEP coal conversion: Fully solar-driven thermo- and electrochemical process for efficient transformation of coal to light fuel plus hydrogen

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ABSTRACT

In this paper, the Solar Thermal Electrochemical Process (STEP) for coal conversion has been successfully introduced and developed for theoretical and experimental demonstration of efficient coal conversion to light fuel with perfectly coupling the solar thermo- and electrochemistry to lift the efficiency of solar utilization and lower endothermic reaction electrolysis potential. By adjusting two chemical processes powered by the solar thermal and electrical fields, the coal was efficiently and selectively converted to light fuel synergistically plus the hydrogen with the sole input of the solar energy and low emission of CO_2. Just because the electricity is integrated into the thermolysis, it has found one way to combine the electrochemistry to the existing coal thermolysis technology so they work more efficiently with the easy selectivity of hydrocarbon fuel and O-containing compounds. The process, characterized with interaction of balancing and controlling the thermal and electrochemical components, provides lower potential and higher efficiency compared with the conventional coal thermolysis. The results show that the yields of the coal gasification and liquefaction were greatly improved with the coupling of thermolysis and electrolysis by reaching 38.5% and 48.8% at 360 °C. The analytical data reveal that the products consist of abundant hydrogen, dominant hydrocarbons and rare O-containing compounds. The yield and selectivity were easily controlled by tuning the temperature and electrolysis current. Based on the results of the experimental analysis, the pathway and mechanism are proposed and explained for the STEP coal conversion process. Due to the combination of the solar thermo- and electrochemical process, this mechanism is shifted from the one reaction of the conventional thermolysis to the dual reaction involving electro-assisted thermolysis and thermo-assisted electrolysis. This study has important implications for the demonstrations of a novel approach of the efficient and energy-saving conversion of coal to light fuel driven by solar energy. The process has realized a transformation of low grade energy to high grade one by the proper utilization of solar energy and rational distribution of the heat and electricity to specific chemical reactions.

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1. Introduction

In recent years, the sharply decreased reserves of fossil fuel and the correspondingly increased pollutions have aroused an increasing attention [1]. Since the nonrenewable fossil fuel is taking up the dominant global energy sources which is burning with a large scale generation of harmful gases, such as CO_2 and SO_2. This facts have altered the global climate and caused the damage of human's health [2]. To meet future energy demands efficiently, energy security and reliability have to be situated on a vital position and alternative energy sources must be investigated with more efforts and investments. With the advent of post-petrochemical industry to renewable energy replacement of oil as the main fuel and raw materials, the research and development of solar-based fuel and chemical processes have intrigued global researchers, which has been raised to the strategy of the scientific research with the significant progress. An effective energy solution should be capable of

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addressing long-term issues by employing alternative and renewable energy sources [3–6]. In future, there will be a diversified production line pattern of the fossil-based and solar-based composite fuel. Intentionally, a research interest should comply with focusing on the utilization of both renewable energy and coal for the production of fuels and chemicals for the post-oil society [7,8].

The solar-based energy has been considered as green fuel for 21 st century with increasing attentions focused on the generation of heat, electricity and fuel. It is becoming the orientations of the low carbon footprint energy development strategy in the future [9–12]. Among the many renewable energy sources, solar energy is clearly a promising option as it is extensively usable. Solar power, especially as it reaches more competitive levels contrasted with other energy sources in terms of cost, may serves the life sustainment of millions underprivileged people and benefits the environment and human beings [13–15]. Currently, the solar applications are most extensively focused on solar to heat and solar to electricity such as solar heater, solar refrigeration and solar to power [16]. In addition, the other applications gained the significant development and improvement for recent advances. The STEP, which originates from the logogram of Solar Thermal Electrochemical Process, has been introduced and developed for a chemical process fully driven by solar energy from a single beam of sunlight on the basis of matching and coupling of the solar-to-heat and solar-to-electricity conversion as distinguished from the thermo-chemistry and electro-chemistry. The theory of the STEP process was introduced in 2009 as an extension of the earlier theory and experiment of efficient solar water splitting [17,18]. From 2010 on, the applications of the process have been presented with the increasing portfolio of societal staples including the portfolio of STEP iron [19,20], STEP carbon capture [21,22], STEP ammonia [23], STEP organic synthesis [24,25], STEP sungas [26], STEP nanofibers [27] and STEP wastewater treatment [28–30] in our past studies.

By owning to the advent of natural gas and other clean energy, coal has quickly become to be an unpopular energy since it can cause pollution. In addition to its direct combustion, coal can be converted into gas, organics and liquids for enhancing the utilization of coal [31,32] by the conventional technologies such as the Direct Coal Liquefaction/Gasification technology (DCL) and Indirect Coal Liquefaction/Gasification (ICL) technology. However, the direct and indirect coal liquefaction/gasification all require complex technologies and external energy provided from other sources.

In this paper, the solar STEP theory and practice are introduced and extended to a novel approach to fully solar-driven and efficient coal conversion to light fuel without any input of energies and with low CO_2 emission, called Solar STEP coal conversion. It is perfectly performed by coupling the solar thermo- and electrochemistry to lift the efficiency of solar utilization and lower endothermic electrolysis potential to produce hydrogen, hydrocarbon and oxygenates. It has revealed that the STEP process can be practiced for production of energetic molecules, conversion of solar energy to solar fuel and efficient improvement of energy grade which transform low grade energy (E.g. coal) to high grade energy (E.g. hydrocarbon fuel and hydrogen fuel). The results demonstrate that the coal gasification and liquefaction can effectively be formatted by the solar STEP coal conversion, and efficiently be operated even at 320 °C (slightly higher than the molten point of the salt electrolyte) under the atmosphere pressure, which greatly lowers the temperature of the traditional coal thermolysis conversion. The process has achieved high efficiencies of both solar utilization and coal conversion with a low endothermic potential of thermos-assisted electrochemistry. To our delight, the high conversion rate of coal by STEP could reach to 87.3% with the current of 0.4 A at 360 °C for 6 h. The gasification rate goes to 38.5% and the liquefaction rate goes to 48.8%. Theoretically and experimentally, it is demonstrated that the STEP coal conversion process opens an effective way to transform coal to fuels and chemicals at high conversion rate and selectivity by matching and balancing the thermal and electrical process of solar energy.

Table 1
Analysis data of coal sample

Proximate analysis $w_t\%$			Ultimate analysis $w_{daf}\%$				
M_{ad}	A_d	V_{daf}	C	H	N	S	O
8.83	22.18	54.26	82.67	5.75	0.88	0.53	10.17

2. Experimental

2.1. Sample preparation

The coal (Shuangyashan, china) was used as the experimental sample and the detailed information of coal was shown in Table.1. The coal was ground into fine particles of less than 80 μm and dried in a vacuum dryer at 105 °C for 24 h. Additionally, the raw coal was digested with aqueous HCl (1:1 by volume) and its ash content was 9.3% calculated by the weightlessness of coal. And then, the coal was washed by HF solution(5% by volume) and its ash content was 3.4%. After that, the sample was needed to be dried to remove water and acid avoiding the disturbance.

2.2. Experimental apparatus and procedures

The main sections of the solar STEP coal conversion experiments are shown in the following subsections in details. Other aspects have been previously described in our papers [25,33,34].

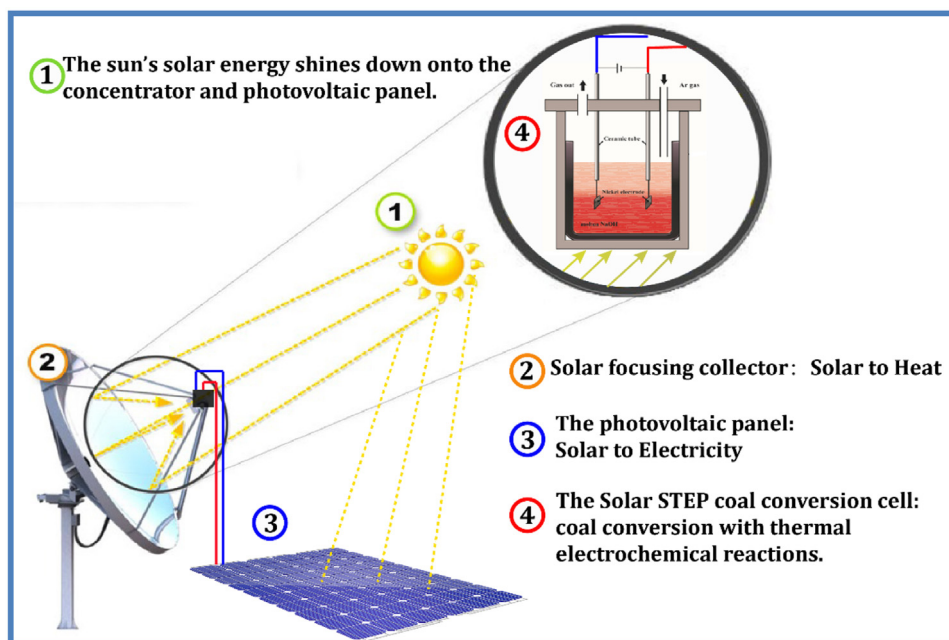#### 2.2.1. Configuration of the thermo-electrochemical reactor

A schematic diagram of the thermo-electrochemical reactor (electrolysis) used in STEP coal conversion experiments is shown in Scheme 1. In this series of experiments, both the anode and cathode are made of polished pure nickel sheets (1.0 × 2.0 cm²) and situated under the surface of the electrolyte. The distance between the anode and cathode was 2 cm. The mixture of pretreated(2 g) coal and electrolyte(NaOH, 20 g) was added into the electrolysis cell (a Ø50*80 mm cell made by corundum). The potential, current, temperature, time and the other conditions were applied and adjusted by the solar photothermic unit and solar photoelectric unit.

2.2.2. Solar photothermic unit for the heat

A solar concentrator was used to match the temperature of the thermo-electrochemical reactor. A parabolic reflector serves to collect energy from parallel incident light and bring it to a single focal point at high temperature (Max.Temp.500 °C). A 1.5 m diameter, parabolic solar concentrator was equipped with 2-dimensional tracking reflector control systems to maintain the solar focus. The reactants filling a reactor was situated at focus point of solar concentrator at temperatures reaching RT−500 °C tuned by the tracking control system.

2.2.3. Solar photoelectric unit for the electrolysis

The silicon-based photovoltaic modules equipped with lithium storage battery were used to convert solar energy into electricity. The solar panels could provide the desired power for electrolysis by simultaneous fine-tuning of the voltage transformer and current transformer. A polycrystalline silicon solar module (3W/18 V, China), consisting of thirty-six (2 × 18) 1.0 cm × 7.8 cm cells, was used for the solar photoelectric unit. The parameters of modules were provided as following: open circuit voltage (V$_{oc}$): 21.8 V; short circuit current (I$_{sc}$): 0.2 A; maximum power voltage (V$_{mp}$): 18 V; maximum power current (I$_{mp}$): 0.17 A; maximum power (P$_{max}$):

Scheme 1. Mode of solar STEP coal conversion experiments.

3 W, and a solar efficiency of 18% under a standard AM (air mass) 1.5 insolation, with the temperature of 25 °C.

2.3. High-temperature cyclic voltammetry analysis

Analysis of high–temperature cyclic voltammetry for coal was performed in thermo- and electrochemical cell by electrochemical working station (CHI650d, Shanghai) at a sweep rate of 20 mV s^{-1} and the potential range was limited between −1.6 V–1.6 V. The polarization time was 2 s at initial voltage. The electrodes were used as described in the above subsection.

2.4. FTIR analysis of the coal samples

The FTIR analysis of before- and after-electrolyzed coals was performed by Fourier transform Infrared Spectroscopy (BRUKER, Tensor 27).

2.5. Analysis of the products

The Multi-dimensional GC (Agilent, 7890B) equipped with TCD and FID detectors was employed for analysis of the gaseous products sampled from the cell. The Multi-dimensional GC can be configured to do an extended natural gas analysis up to C_{14}. The analyzer is a three valves system using 1/8 inch packed columns and a PONA capillary column for the detailed hydrocarbon analysis. The gas sample was obtained during the interval of one hour with a three-minute Ar flow in 50 ml/min. The 150 ml mixture gas was collected in air bag and was injected to the multi-dimensional GC under normal condition to analyze the contents of gaseous products. The volume of contents was calculated according to the external standard method.

The electrolyzed solid residue, firstly, was dissolved with water and filtered to separate the after-electrolyzed coal for the calculation of the total conversion. Then, the filtrating substances were acidified to pH = 3.0 to remove NaOH. The insoluble organic matters were obtained by filtering and drying, and the soluble organic matters were extracted by acetone. Finally, the soluble organic matters were extracted to remove the solvent by rotary evaporation. The

mass of insoluble and soluble organic matters could be used to calculate the liquid conversion. The conversions are calculated by the following equations.

$$\theta_T = \frac{w - w'}{w} \times 100\% \tag{1}$$

$$\theta_L = \frac{w_s + w_i}{w} \times 100\% \tag{2}$$

w − the mass of coal before electrolysis

w' − the mass of coal after electrolysis

w_s − the mass of soluble organic matter

w_i − the mass of insoluble organic matter

In the conversion process, it is considered that there were any solid products converted from original coal. These solid products were very few and hard to analysis and caculate, so we regarded these solid as the residual reactant when calculated the conversion rate. So the gaseous products conversion rate is calculated with:

$$\theta_G = \frac{w' - (w_s + w_i)}{w} \times 100\% \tag{3}$$

The liquid products (insoluble and soluble organic substances) dissolved with benzene (98.5%, purity) were injected into GC (Agilent, 6890N) using a 30 m*0.25 mm*0.33 μm HP-5 column with FID detector. The oven temperature was programmed from 50 °C (5 min hold) to 300 °C (30mins hold) with 10 °C/min heating ramp. The injection port and the detector temperatures were respectively set up to 280 °C and 300 °C, and a 1 μl liquid sample was injected.

The blank experiments for extraction were conducted. The pretreated coal without electrolysis was extracted by benzene via the same process for the blank experiment.

2.6. The high heat value(HHV) of products and the calculations of solar power conversion

2.6.1. The high heat value(HHV) of products

The high heat value(HHV) was used to calculate the solar conversion efficiency in the Section 3.5. In the calculations of solar conversion efficiency, the HHV was divided into two parts, the high heat value of gaseous products and liquid products. We use the given HHV originating from the NIST chemistry webbook to calculate the heat value of known gaseous or liquid components. In additional, the heat value of unknown components could be obtained by experiments with automatic calorimeter (XRY-1C, Shanghai, China). The automatic calorimeter is used to determine the heat value of fuel according to the Chinese national standard GB/T 213–2003 which determines the gross heat value by the bomb calorimetric method. So, the energy of products could be calculated with the heat value of products and the mass or volume of products.

2.6.2. The calculations of solar power conversion

The energy of converted solar power was calculated with the total solar power and the conversion efficiency. The total solar power input was defined with the local amount of direct solar radiation per hour, MJ/m²·h which is calculated by annual amount of direct solar radiation and annual sunshine duration.

$$Q_{sun} = \frac{R_y}{H_y} \times h \times S \times_{STEPsolar} \tag{4}$$

R_y – the annual amount of direct solar radiation, MJ/m^2

H_y – the annual sunshine duration, h

h – the time of experiments, h

S – the cross sectional area of concentrator, m^2

$\eta_{STEPsolar}$ – Solar conversion efficiency of full spectrum sunlight STEP conversion

And the conversion efficiency of solar to heat and solar to electricity could be calculated by full spectrum conversion efficiency (details shown in 3.5).

3. Results and discussion

3.1. Theoretical analysis of the STEP coal conversion

The conventional thermolysis of coal has been currently applied with high temperature, where the endothermic processes are constrained by an input of high energy. Although maintaining a high temperature would be very costly, the sun can easily serve this task. And the solar energy could drive the electrochemical process which could enhance the thermolysis conversion of coal. The high temperature activates the reactants and leads to aggrandizement of electrochemical coal conversion. It is necessary that the thermochemistry is perfectly combined with the electrochemistry for the improvement of solar energy utilization and coal conversion.

In addition to the thermochemical reactions, there are also electrochemical reactions in the STEP coal conversion process. The coal molecules can be oxidized for the splitting to hydrogen and light hydrocarbon and for the oxidation to o-containing compounds on the anode while pure H_2 is generated on the cathode in the same time.

The STEP process is more efficient at higher temperature, because of the lower electrolysis potential. Generally, the heat can decrease the energy to drive an endothermic electrolysis. The process can be described by using data for the available free-energy,
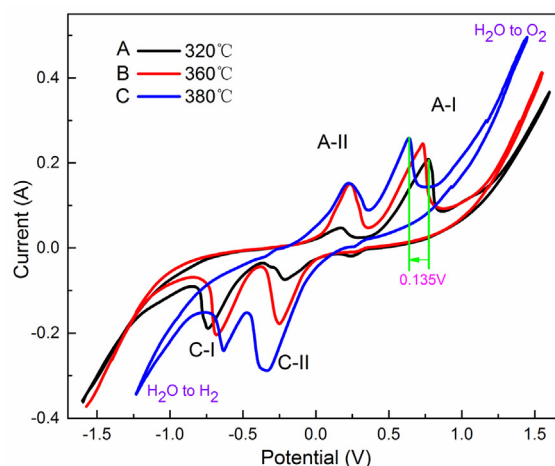

Fig. 1. Cyclic voltammetry of STEP coal conversion with Ni electrodes in molten NaOH at (A)320°C, (B)360°C, (C)380°C at scan rate: 0.03 V s⁻¹.

G, and it is identified by a negative isothermal temperature coefficient of the cell potential. The minimum voltage of electrolytic cell to drive the coal electrolysis is calculated by the Eq. (5):

$$E_{electrolysis} = -\Delta G/nF \tag{5}$$

where, n is stoichiometric coefficient of transited electrons in oxide-reduction reactions, and the Faraday constant, F = 96,500 C mol⁻¹. Thermo corresponding to TΔS can be integrated into the process. The thermoneutral potential, E_{Th}, is given by the enthalpy of coal conversion reaction which the cell operates adiabatically (without heat loss or requirement)

$$E_{Th} = -\Delta H^o/nF \tag{6}$$

E_{Th} is associated to the thermal induced energy when thermal energy be added to assist the electrolysis from solar conversion (high temperature process). The heat from solar conversion makes the entropy changes in the electrolysis process to lower the electrolysis energy ($E_{Th} < E_{electrolysis}$). The electrolysis STEP process is maximized in the opposite temperature domain of the cell, that is, at elevated temperatures that decrease the energy of electrolysis [21]. High temperature is desired as it can lower the energy to drive endothermic electrolysis.

For the STEP coal conversion process, the domains consist of some endothermic reactions. The thermoneutral potentials can been predicted by Eq. (6). The conversion potential will dramatically decrease with the increasing temperature.

3.2. High-temperature cyclic voltammetry of the STEP coal conversion

Maintaining a high temperature is an useful way to get a high electrolysis rates and electrolysis efficiency. The STEP process could drive thermo and electrochemical reactions at the same time with the utilization of solar energy. The coupling of thermolysis and electrolysis of coal gains a better and more efficient way to produce energetic molecules only with the input of solar energy. By matching the thermolysis and electrolysis process, there would be a significant promotion to endothermic reactions and the activates of coal molecules. For further analysis, the couple effect can be well described by high-temperature cyclic voltammetry.

Fig. 1 shows the high-temperature voltammetry of STEP coal conversion reactions at a series of temperatures which indicates that the potential, the electrolysis current, even the reaction pathway, will be greatly varied by increasing the temperature. Two anodic peaks (A-I and A-II) of coal conversion reactions associ-

ated with the endothermic reactions occur with a positive scanning direction and they are both less than the onset potential of the oxygen emission ($H_2O \rightarrow O_2$). This proves that the potentials of coal oxidation are less than that for water oxidation, thus favoring efficient electrooxidation. Furthermore, it should be emphasized that, as coal is a complex blending of organic and inorganic macromolecules, the voltammetry represents the sort of same type redox processes and associated chemical events taking place rather than merely the oxidation of a single solution component.

Fig. 1 also demonstrates that the varied temperature leads to the changes of the anodic oxidation peak potential and current. It is apparent that the anodic oxidation peak (A-I) potential is sharply down while the current increasing with the temperature ascends. This effect is significant for peak A-I, which appears a potential drop of 0.135 V from 320 °C to 380 °C, while this effect is improper at the other peak A-II, which changes of potential have not obvious connection with the increasing temperature. An aim of STEP process is to decrease the potential and increase the current. The results of high-temperature voltammetry have demonstrated that thermal energy can decrease the necessary potential and energy of electrochemical process, and the thermochemistry coupled with electrochemistry changes the mechanism and pathway.

3.3. Conversion and selectivity of STEP coal conversion process

The solar STEP coal conversion process at various current and temperature was investigated. The mass of coal decreased significantly after conversion resulting a total conversion rate of 87.3% with a 0.4A current at 360 °C for 6 h. According to the analysis of products, there were 38.5% solid coal converted to gaseous products and 48.8% solid coal converted to liquid products. The results came from the current and temperature tuning by coupling process of thermolysis and electrolysis.

Fig. 2 presents the sum of the conversion of coal to gaseous products and liquid products under various conditions. We have calculated the total conversion of coal using experimental setup at different temperature and current for 6 h (Fig. 2a). As expected from the CV results and the thermodynamic analysis of STEP coal conversion, the thermal energy is beneficial for the conversion of coal. With ascending currents, the total conversion increases (Fig. 2a), which indicates that the incensement in current improved the conversion of coal. The conversion rate increases with temperature and current, and reaches the maximum values at both the highest temperature (360 °C) and highest current density (0.4 A). Fig. 2b and c are the comparisons of the gaseous and liquid conversion with the respect to the total conversion. It is obvious that the total and liquid conversion increase with temperature and current, but the gaseous conversion changes slightly with the current and even decreases under higher temperature. It could be concluded that the selectivity of the gaseous and liquid conversion changes with temperature and current, in other words, the high selectivity of gaseous or liquid products can be realized through the adjustment of temperature (solar thermochemical process) and electrolysis current (solar electrochemical process). Ultimately, the changes of conversion and the selectivity are attributed to the synergistic effect of solar thermochemical reactions and solar electrochemical reactions.

3.4. Analysis of the STEP coal conversion products

3.4.1. The gaseous products obtained during STEP coal conversion process

The gaseous products formed at anode and cathode were collected and analyzed during the STEP coal conversion process with 0.4A at 360 °C for 6 h. Actual components of gaseous products obtained from electrolysis cell were hydrogen, carbon dioxide and carbon monoxide detected by TCD detector and methane, ethane

and other hydrocarbons detected by FID detector. From Fig. 3a and b, we could conclude that the main components of gaseous products are hydrogen and methane. According to Fig. 3d, the volume of carbon dioxide and increased slightly with the time but were not vast quantities while the volume of hydrogen was plenty which means that we could get an ideal hydrogen generation with very limited CO_2 emissions by STEP Coal conversion process. The results of the evolution of gaseous products at the anode and cathode are shown in Fig. 3d. Meanwhile, the volume of methane decreased with time but the hydrogen increased. At the same time, the generation of other hydrocarbons and carbon monoxide are in small increment. Given these results, we assumed that the STEP coal conversion process could not oxidize the coal directly into CO_2 at anode, and the most possibility was broken up to smaller organic carbon oxides. With the further oxidation, these organics would be oxidized to much smaller molecules, which is considered as the reason for the increasing volume of other hydrocarbons and carbon monoxide.

Furthermore, a set of experiments were performed merely with thermolysis, so as to be compared with the experiments coupling thermolysis and electrolysis to prove the efficient of the STEP coal conversion process. The GC analysis of gaseous products formed during the experiment performed without electrolysis at 360 °C for 6 h shown in Fig. 3a was observed that the components were same as the experiments with electrolysis, but the content of compounds was different and became less and less with time. According to Fig. 3c, it is obviously that the total and gas conversion rate of experiments merely with thermolysis were much lower than that experiments with STEP conversion process. Also from Fig. 3e, by comparisons with Fig. 3d, the volume of gaseous products generated from the experiments merely with thermolysis was much smaller than the experiments coupled with electrolysis, whereas, the thermal effects are limited under such temperature and products were enhanced by the addition of electricity. Through the above analysis and comparisons, we could conclude that the STEP coal conversion process is much more efficient than the process merely with thermolysis.

Additional study on the relationship between changing current and the generation of methane was performed with holding constant cell potential of 1.0 V for 6 h. Considering the changes of current with the time shown in Fig. 4, the current densities increased fast at the beginning, gradually leveled off at about a value, and then drop rapidly, which indicates that the oxidation reactions did occured in the coal under high temperature. The amount of the methane generation subsequently was determined in the course of time and had changed in line with the trends of current evolutions in proceeding of electrolysis (Fig. 4). It is possible that the average oxidation state of coal in experiments changes with the time which implies the changes of coal conversion mechanism varied with time.

3.4.2. The GC analysis of liquid products of solar STEP coal conversion process

After constant current electrolysis of coal at 0.4 A for 6 h under 360 °C, the solid residual was dissolved to water transferring the liquid products to alkaline water slurry, and then the pH of slurry was adjusted to acid range. The liquid products were divided into soluble organic matter and insoluble organic matter, both of them was extracted by benzene and injected into the gas chromatography for further analysis.

By quantitative analysis of liquid products, there were 0.976 g solid coal converted to liquid products from original coal and there were 0.676 g soluble organic matter and 0.291 g insoluble organic matter. Obviously, the coal converted to soluble organic matter is more than to insoluble organic matter, which means there are more generation of Hydrophilic oxidation products. Furthermore, the liq-
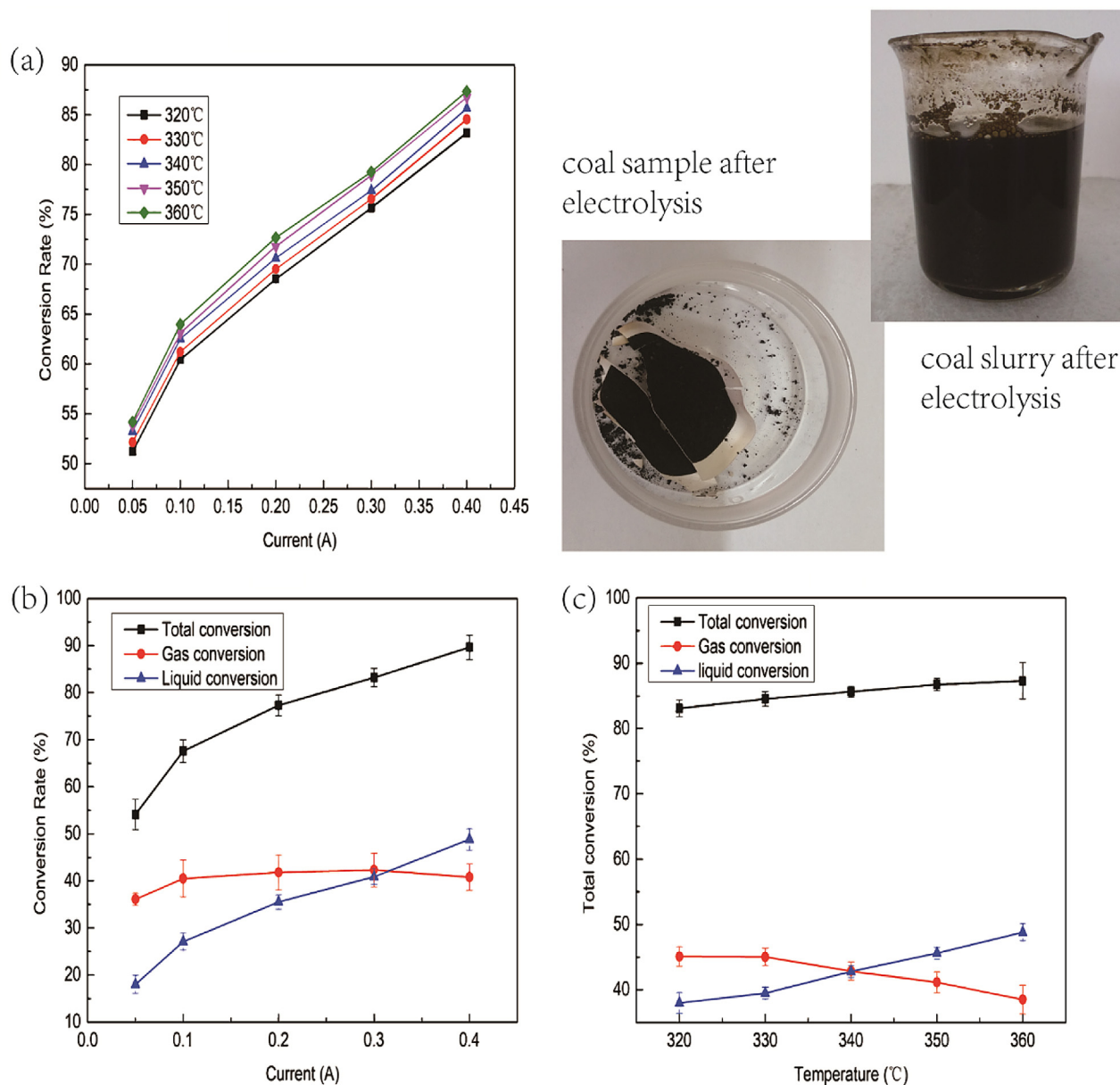
Fig. 2. (a)The total conversion rate at various current with different temperature (b)The conversion rate of STEP coal conversion process in various current at 360 °C(c) The conversion rate of STEP coal conversion process in various temperature at 0.4A.

uid products were analyzed by GC and the results are performed in Fig. 5. This analysis shows that the STEP coal conversion process could provide abundant liquid products. Sample blank experiment emendated disturbance produced from the extraction of raw coal which only the solvent peak appears in chromatomap without other apparent fingerprint peaks. The results after electrolysis are quite different from the blank experiment. The organic matter extracted by benzene in blank experiments was few detected by GC, but the matter extracted after electrolysis is complicated and diversiform. Also the chromatomap indicates that the components of liquid products tend to be distributed in low boiling point region. Based on an analysis of the results, there are 90% detected components driven off in 40 min (300 °C) and 10% driven off in last 30 min which illustrates that the light components constitute a large proportion in detected products.

3.4.3. Infrared analysis of the products of solar STEP coal conversion

Spectral analysis of the liquid product has been probed. As shown in Fig. 6, the FT-IR spectrum of the liquid products after thermolysis and STEP coal conversion process were carried out between 4000 and 400 cm^{-1}. Some spectra changes were observed in coal structure after coal conversion process. The strong 1615 cm^{-1} should be assigned to the C=O stretching vibration band of carboxyl. The peak 1400 cm^{-1} and the board between 3200 and 3554 cm^{-1} are the bending vibration of −OH and the O−H stretching bonds of −COOH. The stretching vibration of bands in 1090 cm^{-1} reveal that the hydroxylation reactions occurred by electrolysis [35] and the bands at 1100 cm^{-1} to 1300 cm^{-1} are attributed to the stretching of −C−O− and C−O−C belonging to the carboxyl group [36]. The deformation peaks of 1307 cm^{-1} and 3016 cm^{-1} are attributable to C−H functional group in aliphatic
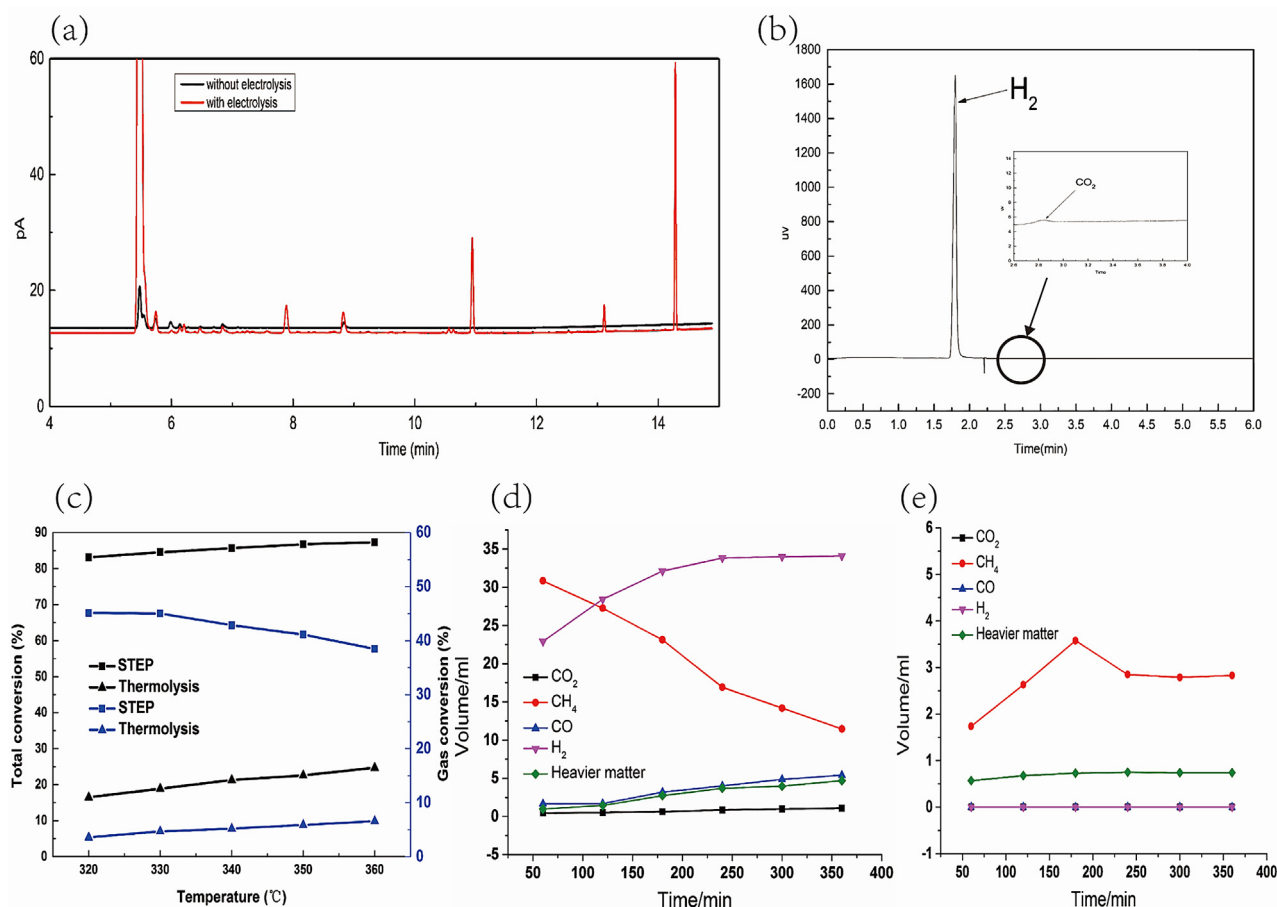
Fig. 3. (a) the GC analysis of gaseous products by FID detector, (b) the GC analysis of gaseous products by TCD detector (c) the total and gas conversion rate of STEP process and merely thermolysis process (d) the contents of gaseous products change with time by STEP in 0.4A at 360 °C for 6 h (e) the contents of gaseous products change with time by thermolysis at 360 °C for 6 h.
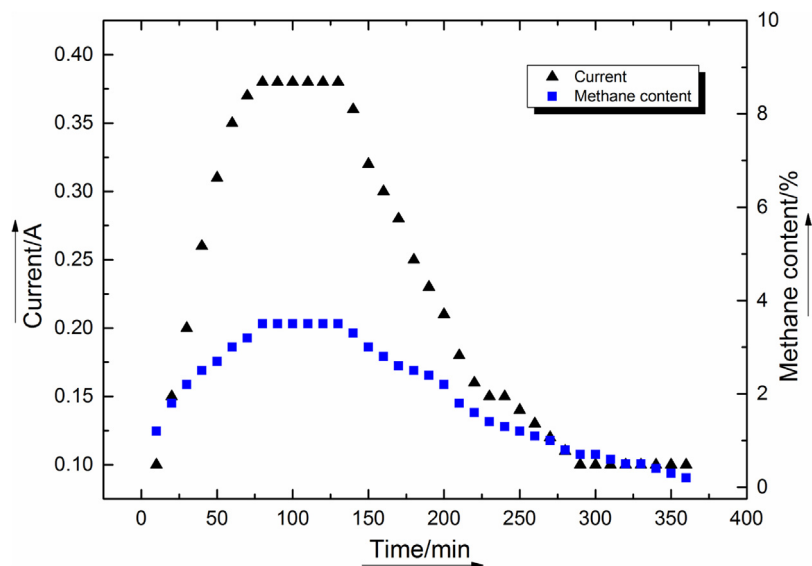

Fig. 4. STEP coal conversion with Ni electrodes in molten NaOH at 1.0 V and methane yield with electrolysis time.

structure and the peak of C=C stretching at 1628 cm^{-1} belongs to the aromatics ring [37].

Compared with the liquid products after STEP coal conversion process, the spectrum of the liquid products after thermolysis just contains some aromatic characteristic peaks. The peaks appear at

845 and 1065 are attributable to the bending stretching of C—H and the stretching C—O on the aromatic branched chain. There are peaks assigned to the C=O and C—O stretching at 1282 and 1640 cm^{-1} too, but not very strong. Together these provided evidences shows that the STEP process get better coal conversion effect and more
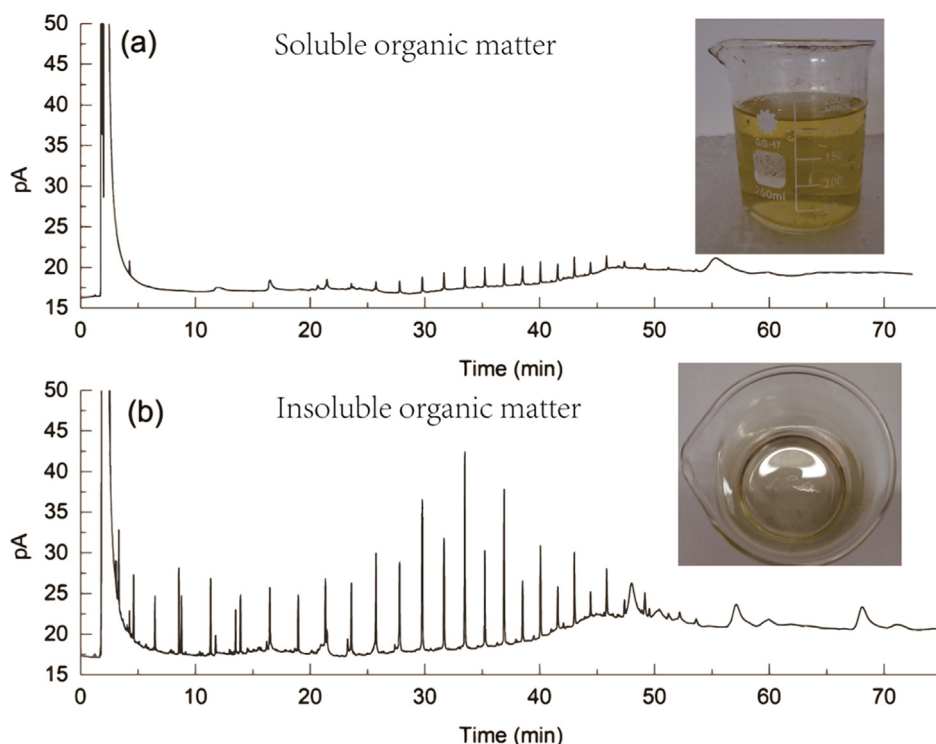
Fig. 5. Gas chromatography (GC) analysis of the liquid products: (a) soluble organic matter (b) insoluble organic matter.
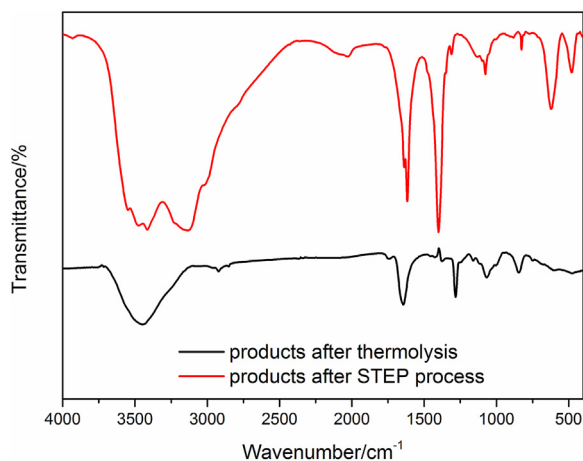

Fig. 6. FT-IR spectrum of the liquid products after thermolysis and STEP coal conversion process.

oxygen functional groups of liquid products than the thermolysis process, which indicates that the combination of thermal and electrochemistry could promote coal conversion reactions and oxidation reactions under thermal environment.

3.5. Efficiency of solar STEP coal conversion process

The utilization of STEP coal process is divided into two parts, solar-energy conversion and chemical reactions. The scheme and program of the solar STEP chemical process and utilization are exhibited in the Scheme 2. Thus scheme indicates that the solar STEP efficiencies are related to the efficiencies of conversion process and chemical reaction. In other words, the overall efficiencies of solar utilization are really depending on the matching and coordination.

The efficiency of a Solar Coal STEP Process:

$$\eta_{STEPsolar} = \eta_{STEPconversion} \times \eta_{STEPchemical} \tag{7}$$

For STEP solar conversion process, there are three conversion approaches, which are solar to photo, solar to electricity and solar to heat. In this STEP coal conversion process, the solar to heat and solar to electricity are selected to drive the chemical reactions. So, the efficiency of solar conversion can be written as:

$$\eta_{STEPsolar} = \eta_{STEPelectro} + \eta_{STEPthermo} \text{ (splitting sunlight)} \tag{8}$$

$$\eta_{STEPsolar} = \eta_{STEPelectro} \times \eta_{STEPthermo} \text{ (full spectrum sunlight)} \tag{9}$$

The efficiency reached to 65–80% of the present maximum value to thermo flux, achieved to 14–40% of the recorded value to electro flux in the present technology [25]. In our experiment section, we establish a full spectrum solar conversion system with a solar panel to power the electrolysis cell with the efficiency of 18–20% and a solar concentrating collector to provide heat with the efficiency of 85%. The full spectrum conversion efficiency is 17%.
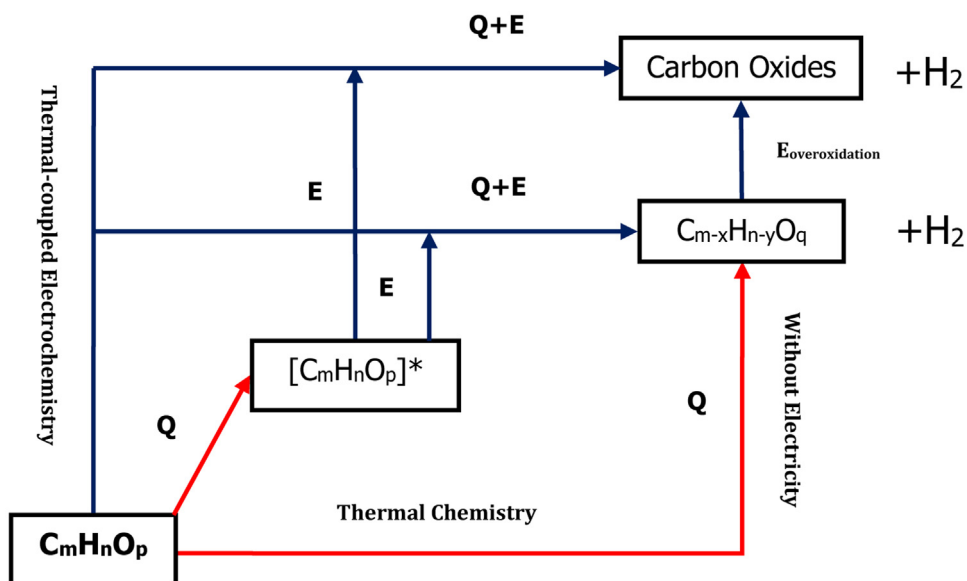
The STEP chemical process takes advantages of both thermo- and electro-chemical process, they have the promotion and could induce the proceeding to each other. So the efficiency of STEP chemical reaction should be:

$$\eta_{STEPcoupled\ electro-and\ thermochem} = \eta_{STEPelectro-induced\ thermochem}$$

$$+\eta_{STEPthermo-inducedelectrochem} \tag{10}$$

After the STEP chemical process in 0.4 A at 360 °C for 6 h, we achieved the electrolysis gaseous product comprised of 55.5% hydrogen, 23.6% methane and 8.4% longer hydrocarbon by volume (calculated with the GC results) and the liquid products comprised of 32% insoluble organic matter and 68% soluble organic matter by weight (calculated by the mass of the products). The products of interest (hydrogen, hydrocarbon, O-compounds) not only produced from the electrolysis process but also from the thermo-

Scheme 2. Scheme and program of the solar STEP coal conversion process and utilization.

Scheme 3. Reaction routes of the solar STEP conversion process: Here two routes in scheme represent the thermal chemical process and the coupling thermo- and electrochemical process respectively. The single use of solar thermal chemistry cannot get effective oxidation on coal in such temperature, while the coupling of it with solar electrochemistry could extend the reactions to gain even more new products and co-product hydrogen.

chemical process. And analysis from the equations, the efficiency of chemical reaction is higher than the efficiency of independent thermo- or electro-chemical reaction. We could conclude that the solar STEP coal process is getting a high efficiency of STEP chemical process.

$$\eta_{STEPcoupled\ electro-and\ thermochem} > \eta_{Independent\ thermochem}\ or\ \eta_{Independent\ electrochem} \quad (11)$$

It is summarized that the efficiency of the solar STEP coal conversion process is:

$$\eta_{STEPsolar} = \eta_{STEPconersion} \times \eta_{STEPchemical} = \left(\eta_{STEPelectro} + \eta_{STEPthermo}\right)$$
$$\times \eta_{STEP\ coupled\ electro-and\ thermochem}\ (splitting\ sunlight) \quad (12)$$

$$\eta_{STEPsolar} = \eta_{STEPconersion} \times \eta_{STEPchemical} = \left(\eta_{STEPelectro} \times \eta_{STEPthermo}\right)$$
$$\times \eta_{STEPcoupled\ electro-and\ thermochem}\ (full\ spectrum) \quad (13)$$

We also calculated the conversion efficiency of solar to fuel in which only primary solar energy was used for the entire conversion process. The solar to fuel (heat and electricity to fuel) conversion efficiency, η_{SFE}, is defined as:

$$\eta_{SFE} = \frac{HHV_P - Q_{coal}}{Q_{sun}} \quad (14)$$

where HHV_P is the higher heating values of products, Q_{coal} is the higher heating values of the consumed coal and Q_{sun} is the solar power converted to heat and electricity. By calculation, the efficiency of solar energy to fuel is 11.86%. For present experiments, the mode of solar energy utilization is full spectrum, if we change it to splitting sunlight, the efficiency of solar to fuel could gain great growth. Equally important, all major losses and inefficiencies in the conversion process are also should be considered, and the decreasing of energy loss and inefficiency could promote the process of solar to fuel.
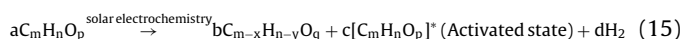
General analysis is contributed to show that the solar STEP coal conversion process is an efficient way to enhance the solar utilization and the efficiency of chemical reactions.

3.6. The mechanistic pathways for STEP coal conversion process

3.6.1. The coupling process of the solar thermo- and electrochemical reaction

The changes of structure and the difference of functional groups described a mechanism pathway of STEP coal conversion. For common recognition, the coal contains organic and inorganic materials, and the main constitutes of the organic part is Polycyclic Aromatic Hydrocarbons (PAHs) which is complicated with high molecule weight and high-rings. The dominant elements of coal are C, H, O by descending order of the content [38]. Considering the chemical structure and the composition of coal, the coal-related model compound could be expressed by $C_mH_nO_p$. In the STEP coal conversion system with high temperature, the reactions were dominated by thermochemical reactions, electrochemical reactions and the concerted reactions of them.
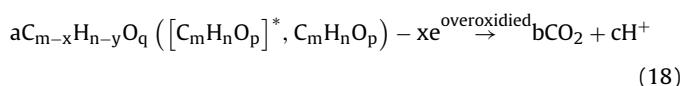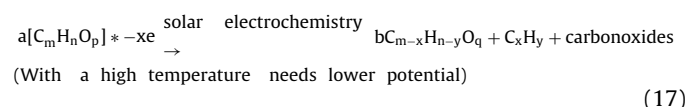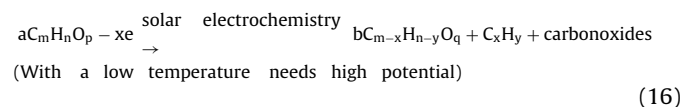
By studying the gaseous products of the thermolysis without electricity at 360 °C and eliminating the effect of small molecule hydrocarbon absorbed in pore, the solar heating effect enhanced the coal intermolecular interactions and made the molecule in activated state and a small part of organics thermal cracked. The solar thermochemical reaction of the STEP coal is:

$$aC_mH_nO_p \xrightarrow{solar\ electrochemistry} bC_{m-x}H_{n-y}O_q + c[C_mH_nO_p]^*\ (Activated\ state) + dH_2 \quad (15)$$

Coupled with the electrochemical reactions, the gaseous products were quite different from the solar thermolysis. According to the results of the gaseous content, the generation of small molecule hydrocarbon was efficient. The electrochemical oxidation could not oxidize the coal directly into CO_2, and the most possible to be broken up to smaller molecule organics. With the further oxidation, these molecules would be oxidized to much smaller molecules and will be eventually oxidized to dioxide carbon with long enough time. It is a coupling process shown in Scheme 3 with thermo- and electrochemistry that they are not isolated, on the contrary, they complement each other. The electrochemical reaction of the STEP coal conversion process is:
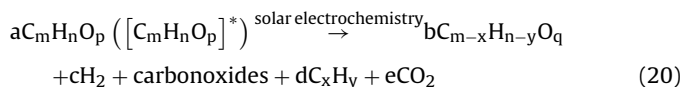
At the anode:

$$aC_mH_nO_p - xe \xrightarrow[\rightarrow]{solar\quad electrochemistry} bC_{m-x}H_{n-y}O_q + C_xH_y + carbonoxides$$
$$(With\ a\ low\ temperature\ needs\ high\ potential) \quad (16)$$

$$a[C_mH_nO_p]* - xe \xrightarrow[\rightarrow]{solar\quad electrochemistry} bC_{m-x}H_{n-y}O_q + C_xH_y + carbonoxides$$
$$(With\ a\ high\ temperature\ needs\ lower\ potential) \quad (17)$$

$$aC_{m-x}H_{n-y}O_q\left(\left[C_mH_nO_p\right]^*, C_mH_nO_p\right) - xe \xrightarrow{overoxidied} bCO_2 + cH^+ \quad (18)$$

At the cathode:

$$2H^+\left(OH^-\right) + 2e \rightarrow H_2 \quad (19)$$

Net reaction:

$$aC_mH_nO_p\left(\left[C_mH_nO_p\right]^*\right) \xrightarrow{solar\ electrochemistry} bC_{m-x}H_{n-y}O_q$$
$$+ cH_2 + carbonoxides + dC_xH_y + eCO_2 \quad (20)$$

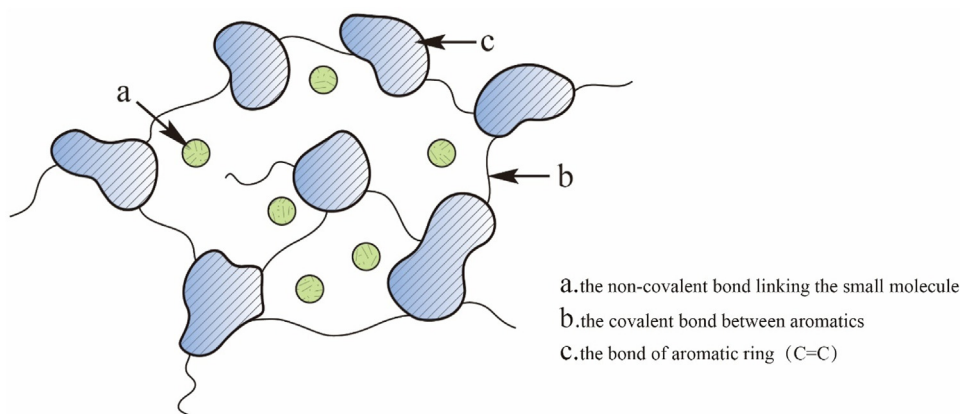#### 3.6.2. Looking for the mechanism pathway by structure of coal

Van krevelen [39] proposed a theory about structure of coal first. Many structure models of coal were developed and researched, and among these models, the Host-Guest model is more representative [40]. In the theory of Host-Guest model of coal, the cross linked macro molecule of coal is considered to be stationary phase and the small molecule inserted into the macro molecule structure with non-covalent bond is considered to be mobile phase (Scheme 4). In other words, the macro molecule such as poly-aromatics is the Host and the small molecule is the Guest [41]. A view of the structure is illustrated that there is a number of different types of reactive sites, which are susceptible to be oxidized. According to the characteristics of the structure, the reactive sites are located in three different areas of coal.

It can be considered that the kinetics of coal conversion would be influenced by the activity of reactions on these different reactive sites, resulting in different intensity for oxidation of the different sites on the Host-Guest structure. By solar thermal energy, the Guest (small molecule) and part of the Host (the aromatic macromolecules) were both transformed into excitation state. With the collection of formed small gases molecules, the observations indicate a significant reduction of energy to break the non-covalent bond (a) linking with the small molecules in excitation state. At the longer times of the process, the break occurred at the covalent bond (b) between aromatic molecules (ether bond, ester bond). Analysis with the products and the coupling of the thermal- and

a. the non-covalent bond linking the small molecule
b. the covalent bond between aromatics
c. the bond of aromatic ring (C=C)

Scheme 4. "Host-Guest" coal physical structure model with three types of reactive sites: a) the non-covalent bond linking the small molecule, b) the covalent bond between aromatics, c) the bond of aromatic ring(C=C).

electrochemical process, the functional groups present at the covalent bond between aromatics became more active by solar thermal energy and were broken by electrolysis. Reactions occurring on the bond of aromatic ring (c) were so hard that the reactions may occur after prolonged oxidation and need a large scale of energy. The bond of aromatics oxidized with time may break into the covalent (a) and non-covalent bond (b) by the cracking of aromatic rings.

4. Conclusions

The purpose of this study was to transform coal into light fuel and chemicals plus hydrogen by STEP coal conversion process which driven by solar energy without inputting any other forms of energy and chemicals. STEP can be used to utilize the efficiency of conversion and selectivity on converting coal to light fuels at 87.3%, generating the gasification products at 38.5% and liquefaction products at 48.8% with a lower temperature 360 °C under atmosphere pressure. The STEP coal conversion process is characterized to be an efficient and sustainable process for enhancing the utilization of coal. Our finding indicates an energy-conversion system, transforming the low grade energy (fossil fuel) to high grade energy (hydrocarbon fuels and chemicals) through the sustainable & renewable solar energy.

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